Supporting Information for

Iridium-Catalyzed Intramolecular Asymmetric Allylic Etherification of Salicylic Acid Derivatives with Chiral-Bridged Biphenyl Phosphoramidite Ligands

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Table of Contents:

1. General considerations .................................................................................................................. S1
2. Table S1 Optimization of Reaction Conditions ........................................................................... S2
3. Experimental Procedures ............................................................................................................. S3
   3.1 General Procedure for the Synthesis of Salicylic Acid Derivatives 1 ............................. S3
   3.2 General Procedure for the Allylic Etherification of 1 ..................................................... S15
   3.3 Gram-scale Reaction ........................................................................................................ S30
   3.4 Procedure for the Synthesis of 3v .................................................................................. S30
   3.5 Procedure for the Synthesis of 3a ................................................................................ S31
   3.6 Procedure for the Synthesis of 4a ................................................................................ S32
4. Copies of NMR Spectra ............................................................................................................. S35
5. Copies of HPLC Chromatograms ............................................................................................. S86
6. X-ray Crystallographic Data .................................................................................................... S111
1. General considerations

Unless otherwise stated, all syntheses and manipulations of air- and moisture-sensitive materials were carried out in a nitrogen-filled glovebox or under nitrogen atmosphere using standard Schlenk techniques. All glassware was oven-dried immediately prior to use. All solvents were freshly distilled and degassed according to standard methods. Reactions were magnetically stirred and monitored by analytical thin-layer chromatography (TLC). TLC was performed on Merck silica gel 60 F254 TLC glass plates and visualized by exposure to ultraviolet light. Organic solutions were concentrated by rotary evaporation at 20 – 45 °C.

All chemicals and reagents available from commercial sources were directly used without further purification. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (200 – 300 mesh). $^1\text{H}$, $^{19}\text{F}$, and $^{13}\text{C}$ NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer at ambient temperature. High-resolution mass spectra (HRMS) were obtained with Shimazu LC-20AT mass spectrometer. Optical rotations were measured on SGW®-5 automatic polarimeter. Enantiomeric excesses (ee values) of the products were determined by chiral HPLC analysis using an Aglient HP 1200 instrument (n-hexane/2-propanol as eluent) with a Chiralpak IF-3 or IA-3 Column. The phosphoramidite ligands L$^1$ – L$^8$ were prepared according to the reported procedures.
2. Table S1 Optimization of Reaction Conditions

![Reaction Scheme](image)

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*a* Conditions: [Ir(cod)Cl]2 (4 mol %), ligand (8 mol %), base (0.2 mmol), and 1a (0.1 mmol) in solvent (2.0 mL). *b* Isolated yields. *c* Determined by chiral HPLC analysis. *d* 2 mol % of Ir catalyst was used. *e* 1 mol % of Ir catalyst was used.
3. Experimental Procedures

3.1 General Procedure for the Synthesis of Salicylic Acid Derivatives 1

To a solution of substituted salicylic acids 5 (2 mmol, 1.0 equiv.) in DMF (10 mL), 1-hydroxybenzotriazole (HOBT) (297 mg, 2.2 mmol, 1.1 equiv.) and N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDC·HCl) (422 mg, 2.2 mmol, equiv.) were added. This mixture was stirred for 30 minutes at room temperature, then compounds 6 (2 mmol, 1.0 equiv.) was added. After the reaction was complete (monitored by TLC), the crude reaction mixture was diluted with EtOAc (20 mL) and washed with water (10 mL x 3) and brine (15 mL x 3). The combined organic layers were dried over Na₂SO₄. Afterwards, the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum/EtOAc = 3 : 1) to afford the desired compounds 1.
(E)-4-(N-benzyl-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1a)

Yellow oil, 0.67 g, 95% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.78 (s, 1H), 7.47 – 7.26 (m, 7H), 7.05 (d, $J = 8.2$ Hz, 1H), 6.80 (t, $J = 7.4$ Hz, 1H), 5.91 (m, 1H), 5.83 – 5.65 (m, 1H), 4.76 (s, 2H), 4.69 (d, $J = 5.2$ Hz, 2H), 4.09 (d, $J = 4.8$ Hz, 2H), 3.83 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.42, 159.09, 155.52, 136.13, 132.93, 129.39, 128.95, 127.77, 127.55, 127.43, 118.65, 118.28, 118.19, 117.06, 67.29, 54.92. HRMS (ESI) calcd for C$_{20}$H$_{21}$NO$_5$ [M+H]$^+$: 356.1493, Found: 356.1485.

(E)-4-(N-benzyl-2-hydroxy-4-methylbenzamido)but-2-en-1-yl methyl carbonate (1b)

Yellow oil, 0.63 g, 85% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 10.01 (s, 1H), 7.43 – 7.27 (m, 5H), 7.21 (d, $J = 8.0$ Hz, 1H), 6.85 (s, 1H), 6.60 (d, $J = 7.9$ Hz, 1H), 5.91 (m, 1H), 5.83 – 5.70 (m, 1H), 4.75 (s, 2H), 4.69 (d, $J = 5.5$ Hz, 2H), 4.07 (d, $J = 5.1$ Hz, 2H), 3.83 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.64, 159.39, 155.53, 143.93, 136.24, 129.52, 128.93, 127.71, 127.43, 127.36, 119.62, 118.46, 114.04, 67.33, 54.92, 21.54. HRMS (ESI) calcd for C$_{21}$H$_{23}$NO$_5$ [M+H]$^+$: 370.1649, Found: 370.1643.
(E)-4-(N-benzyl-2-hydroxy-5-methylbenzamido)but-2-en-1-yl methyl carbonate (1c)

Yellow oil, 0.61 g, 83% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (m, 5H), 7.20 – 7.09 (m, 2H), 6.94 (d, $J = 8.4$ Hz, 1H), 5.96 – 5.85 (m, 1H), 5.82 – 5.71 (m, 1H), 4.75 (s, 2H), 4.69 (d, $J = 5.5$ Hz, 2H), 4.08 (d, $J = 5.0$ Hz, 2H), 3.83 (s, 3H), 2.19 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.41, 156.24, 155.54, 136.29, 133.47, 129.63, 128.89, 127.89, 127.72, 127.57, 127.44, 117.82, 117.33, 67.33, 54.91, 20.42. HRMS (ESI) calcd for C$_{21}$H$_{23}$NO$_5$ [M+H]$^+$: 370.1661, Found: 370.1642.

(E)-4-(N-benzyl-2-hydroxy-6-methylbenzamido)but-2-en-1-yl methyl carbonate (1d)

Yellow oil, 0.63 g, 85% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.27 (m, 5H), 7.21 (d, $J = 8.0$ Hz, 1H), 6.85 (s, 1H), 6.60 (d, $J = 7.8$ Hz, 1H), 5.90 (m, 1H), 5.77 (m, 1H), 4.75 (s, 2H), 4.69 (m, 2H), 4.08 (d, $J = 8.0$ Hz, 2H), 3.83 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.44, 155.57, 152.88, 135.48, 129.98, 128.69, 128.36, 127.66, 122.00, 114.21, 67.41, 54.90, 19.14. HRMS (ESI) calcd for C$_{21}$H$_{23}$NO$_5$ [M+H]$^+$: 370.1661, Found: 370.1642.
\((E)-4-(N\text{-benzyl-2-hydroxy-3-methoxybenzamido})\text{but-2-en-1-yl methyl carbonate (1e)}\)

Yellow oil, 0.72 g, 93% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32 (m, 5H), 6.92 (d, \(J = 3.7\) Hz, 2H), 6.86 (d, \(J = 7.1\) Hz, 1H), 5.82 (m, 1H), 5.72 (m, 1H), 4.68 (s, 2H), 4.65 (d, \(J = 4.0\) Hz, 2H), 3.99 (d, \(J = 4.0\) Hz, 2H), 3.92 (s, 3H), 3.82 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.23, 155.54, 147.60, 144.55, 136.49, 129.92, 128.74, 127.69, 127.56, 126.90, 120.91, 119.65, 119.57, 112.47, 67.47, 56.19, 54.89, 53.44. HRMS (ESI) calcd for C\(_{21}\)H\(_{23}\)NO\(_6\) [M+H]\(^+\): 386.1610, Found: 386.1588.

\((E)-4-(N\text{-benzyl-2-hydroxy-4-methoxybenzamido})\text{but-2-en-1-yl methyl carbonate (1f)}\)

Yellow oil, 0.56g, 73% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 (m, 6H), 6.55 (d, \(J = 2.3\) Hz, 1H), 6.33 (dd, \(J = 8.7, 2.1\) Hz, 1H), 5.92 (m, 1H), 5.85 – 5.71 (m, 1H), 4.74 (s, 2H), 4.69 (d, \(J = 8.0\) Hz, 2H), 4.08 (d, \(J = 4.0\) Hz, 2H), 3.83 (s, 3H), 3.82 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 172.85, 163.52, 162.36, 155.52, 136.29, 129.58, 128.94, 127.70, 127.42, 108.94, 105.95, 102.06, 67.33, 55.37, 54.90, 50.79, 48.76. HRMS (ESI) calcd for C\(_{21}\)H\(_{23}\)NO\(_6\) [M+H]\(^+\): 386.1610, Found: 386.1589.
**(E)-4-(N-benzyl-2-hydroxy-5-methoxybenzamido)but-2-en-1-yl methyl carbonate (1g)**

Yellow oil, 0.67 g, 87% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.41 – 8.94 (m, 1H), 7.37 (m, 5H), 6.93 (m, 3H), 6.11 – 5.71 (m, 2H), 4.76 (s, 2H), 4.70 (d, $J$ = 4.0 Hz, 2H), 4.10 (m, 2H), 3.83 (s, 3H), 3.51 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.20, 155.54, 152.50, 151.77, 136.29, 129.45, 128.98, 127.74, 127.51, 127.24, 119.87, 118.94, 117.40, 111.21, 67.29, 55.52, 54.90, 48.50. HRMS (ESI) calcd for C$_{21}$H$_{23}$NO$_6$ [M+H]$^+$: 386.1610, Found: 386.1589.

**(E)-4-(N-benzyl-2-hydroxy-6-methoxybenzamido)but-2-en-1-yl methyl carbonate (1h)**

Brown oil, 0.67 g, 87% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (s, 1H), 7.26 (m, 6H), 6.57 (d, $J$ = 8.0 Hz, 1H), 6.43 (d, $J$ = 7.4 Hz, 1H), 5.80 (m, 1H), 5.74 – 5.45 (m, 1H), 4.86 – 4.21 (m, 4H), 3.79 (m, 8H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.86, 156.43, 156.35, 156.33, 156.01, 155.96, 155.91, 155.88, 155.62, 155.57, 136.55, 136.38, 136.33, 131.14, 131.11, 130.47, 129.63, 128.57, 127.89, 127.84, 127.59, 127.25, 127.22, 125.83, 111.70, 111.60, 110.12, 102.30, 67.85, 67.34, 55.55, 54.85, 52.15, 49.62, 47.15, 44.78. HRMS (ESI) calcd for C$_{21}$H$_{23}$NO$_6$ [M+H]$^+$: 386.1610, Found: 386.1589.
(E)-4-(N-benzyl-4-fluoro-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1i)

Brown oil, 0.64 g, 86% yield; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.46 (s, 1H), 7.47 – 7.28 (m, 6H), 6.73 (m, 1H), 6.51 (m, 1H), 5.91 (m, 1H), 5.83 – 5.73 (m, 1H), 4.74 (s, 2H), 4.69 (d, \(J = 8.0\) Hz, 2H), 4.07 (d, \(J = 4.9\) Hz, 2H), 3.83 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 171.99, 162.95 (d, \(J = 221.0\) Hz), 161.71, 155.52, 135.94, 129.16 (dd, \(J = 15.8, 12.0\) Hz), 127.77 (d, \(J = 16.6\) Hz), 127.37, 113.19, 106.30, 106.08, 105.37, 105.14, 67.23, 54.92, 50.68, 48.70. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -105.28. HRMS (ESI) calcd for C\(_{20}\)H\(_{20}\)FNO\(_5\) [M+H]\(^+\): 374.1409, Found: 374.1390.

(E)-4-(N-benzyl-5-fluoro-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1j)

Brown oil, 0.64 g, 86% yield; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43 – 7.28 (m, 5H), 7.03 (m, 3H), 5.90 (m, 1H), 5.86 (m, 1H), 4.73 (s, 2H), 4.69 (d, \(J = 4.0\) Hz, 2H), 4.06 (d, \(J = 4.9\) Hz, 2H), 3.83 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 171.11, 155.52, 154.95 (d, \(J = 237.0\) Hz), 154.57, 135.80, 129.05 (d, \(J = 8.9\) Hz), 127.91, 127.61 (d, \(J = 23.4\) Hz), 119.80, 119.57, 119.23 (d, \(J = 7.6\) Hz), 117.92, 113.54, 113.30, 67.19, 54.93, 50.41, 48.58. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -124.04. HRMS (ESI) calcd for C\(_{20}\)H\(_{20}\)FNO\(_5\) [M+H]\(^+\): 374.1409, Found: 374.1392.
(E)-4-(N-benzyl-4-chloro-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1k)

Brown oil, 0.57 g, 73% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.13 (s, 1H), 7.46 – 7.25 (m, 6H), 7.03 (d, $J = 1.4$ Hz, 1H), 6.78 (d, $J = 8.1$ Hz, 1H), 5.88 (m, 1H), 5.83 – 5.70 (m, 1H), 4.72 (s, 2H), 4.68 (d, $J = 8.0$ Hz, 2H), 4.06 (d, $J = 4.8$ Hz, 2H), 3.83 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.70, 159.81, 155.52, 138.37, 135.87, 129.08, 129.01, 128.37, 127.87, 127.71, 127.41, 119.12, 118.35, 115.87, 115.83, 67.22, 54.93, 50.67, 48.62. HRMS (ESI) calcd for C$_{20}$H$_{20}$ClNO$_5$ [M+H]$^+$: 390.1114, Found: 390.1094.

(∑) 4-(N-benzyl-5-chloro-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1l)

Brown oil, 0.5 g, 64% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.60 (s, 1H), 7.46 – 7.23 (m, 7H), 6.97 (d, $J = 8.5$ Hz, 1H), 5.89 (m, 1H), 5.79 (m, 1H), 4.73 (s, 2H), 4.69 (d, $J = 4.0$ Hz, 2H), 4.06 (d, $J = 5.2$ Hz, 2H), 3.91 – 3.66 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.01, 157.15, 155.52, 135.79, 132.60, 129.02, 129.00, 127.92, 127.85, 127.58, 127.04, 123.58, 119.53, 118.68, 67.18, 54.94, 50.52, 49.00. HRMS (ESI) calcd for C$_{20}$H$_{20}$ClNO$_5$ [M+H]$^+$: 390.1114, Found: 390.1093.
(E)-4-(N-benzyl-5-bromo-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1m)

Pale yellow oil, 0.81 g, 93% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.49 (s, 1H), 7.32 (m, 7H), 6.83 (d, \(J = 8.7\) Hz, 1H), 5.88 – 5.79 (m, 1H), 5.78 – 5.68 (m, 1H), 4.69 (s, 2H), 4.65 (d, \(J = 8.0\) Hz, 2H), 4.01 (m, 2H), 3.81 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.60, 156.21, 155.53, 135.87, 134.86, 129.94, 129.10, 128.92, 127.84, 127.70, 120.91, 119.61, 110.73, 67.23, 60.45, 54.92, 48.59. HRMS (ESI) calcd for C\(_{20}\)H\(_{20}\)BrNO\(_5\) [M+H]\(^+\): 434.0609, Found: 434.0589.

(E)-4-(N-benzyl-2-hydroxy-4-nitrobenzamido)but-2-en-1-yl methyl carbonate (1n)

Brown oil, 0.74 g, 92% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.79 (d, \(J = 1.8\) Hz, 1H), 7.66 (d, \(J = 8.0\) Hz, 1H), 7.47 – 7.25 (m, 6H), 5.84 (m, 1H), 5.77 (m, 1H), 4.70 (s, 2H), 4.67 (d, \(J = 4.0\) Hz, 2H), 4.02 (d, \(J = 3.7\) Hz, 2H), 3.83 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.11, 157.71, 155.44, 149.86, 135.44, 129.04, 128.63, 128.10, 128.04, 127.93, 113.87, 112.84, 67.15, 54.98. HRMS (ESI) calcd for C\(_{20}\)H\(_{20}\)N\(_2\)O\(_7\) [M+H]\(^+\): 401.1355, Found: 401.1335.
(E)-4-(N-benzyl-2-hydroxy-4-(trifluoromethyl)benzamido)but-2-en-1-yl methyl carbonate (1o)

Pale yellow oil, 0.8 g, 95% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.85 (s, 1H), 7.48 – 7.36 (m, 4H), 7.28 (d, $J = 9.3$ Hz, 3H), 7.06 (d, $J = 7.3$ Hz, 1H), 5.88 (m, 1H), 5.77 (m, 1H), 4.73 (s, 2H), 4.68 (d, $J = 8.0$ Hz, 2H), 4.06 (m, 2H), 3.83 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.97, 158.26, 155.53, 135.68, 134.35, 134.02, 129.04, 128.88, 127.95, 127.93, 127.81, 124.65, 121.94, 121.18, 115.33 (dd, $J = 25.2$, 3.7 Hz), 67.20, 58.45, 54.96, 53.43. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -63.51. HRMS (ESI) calcd for C$_{21}$H$_{20}$F$_3$NO$_5$ [M+H]$^+$: 424.1378, Found: 424.1357.

(E)-4-(N-benzyl-3-hydroxy-2-naphthamido)but-2-en-1-yl methyl carbonate (1p)

Pale yellow oil, 0.75 g, 92% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (s, 1H), 7.65 (d, $J = 8.2$ Hz, 1H), 7.50 – 7.29 (m, 9H), 5.93 (m, 1H), 5.85 – 5.76 (m, 1H), 4.80 (s, 2H), 4.70 (d, $J = 5.3$ Hz, 2H), 4.13 (m, 2H), 3.84 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.82, 155.56, 153.80, 136.14, 135.86, 129.43, 128.96, 128.44, 127.99, 127.82, 127.57, 126.96, 126.32, 123.99, 120.72, 112.17, 67.30, 54.93. HRMS (ESI) calcd for C$_{24}$H$_{23}$NO$_5$ [M+H]$^+$: 406.1665, Found: 406.1642.
(E)-4-(N-benzyl-3-hydroxyisonicotinamido)but-2-en-1-yl methyl carbonate (1q)

Yellow oil, 0.67 g, 87% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (s, 1H), 8.13 (s, 1H), 7.45 – 7.23 (m, 6H), 5.76 (m, 2H), 4.66 (s, 2H), 4.64 (m, 2H), 4.04 (m, 2H), 3.83 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.25, 155.49, 150.99, 139.67, 138.55, 135.84, 130.62, 128.80, 127.78, 121.94, 67.18, 60.43, 54.89, 53.49. HRMS (ESI) calcd for C$_{19}$H$_{20}$N$_{2}$O$_{5}$ [M+H]$^+$: 357.1455, Found: 357.1438.

(1r)

Yellow oil, 0.75 g, 86% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.17 (s, 1H), 7.53 (s, 1H), 7.45 – 7.29 (m, 9H), 7.04 (d, $J = 7.9$ Hz, 1H), 5.93 (m, 1H), 5.79 (m, 1H), 4.78 (s, 2H), 4.71 (d, $J = 5.1$ Hz, 2H), 4.11 (d, $J = 4.4$ Hz, 2H), 3.84 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.34, 159.85, 155.53, 140.96, 140.25, 136.15, 129.38, 128.99, 128.02, 127.78, 127.58, 126.52, 126.09, 121.79, 116.74, 115.58, 115.34, 67.31, 54.93. HRMS (ESI) calcd for C$_{24}$H$_{23}$NO$_{5}$S [M+H]$^+$: 438.1386, Found: 438.1361.
(E)-4-(N-benzyl-4-(furan-2-yl)-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1s)

Brown oil, 0.78 g, 93% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.51 (s, 1H), 7.37 (m, 7H), 7.11 (d, $J = 8.1$ Hz, 1H), 6.73 (s, 1H), 6.50 (s, 1H), 5.93 (m, 1H), 5.79 (m, 1H), 4.77 (s, 2H), 4.70 (d, $J = 5.2$ Hz, 2H), 4.10 (d, $J = 4.7$ Hz, 2H), 3.84 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.31, 159.83, 155.53, 152.71, 143.00, 136.11, 135.05, 129.35, 128.98, 128.03, 127.78, 127.61, 127.40, 115.31, 114.07, 112.80, 111.90, 107.15, 67.29, 54.93. HRMS (ESI) calcd for C$_{24}$H$_{23}$NO$_6$ [M+H]$^+$: 422.1614, Found: 422.1591.

(E)-4-(N-benzyl-2-hydroxy-4-(6-methoxypyridin-3-yl)benzamido)but-2-en-1-yl methyl carbonate (1t)

Yellow oil, 0.8 g, 87% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.38 (s, 1H), 7.78 (d, $J = 8.5$ Hz, 1H), 7.43 – 7.28 (m, 6H), 7.19 (s, 1H), 6.96 (d, $J = 7.7$ Hz, 1H), 6.82 (d, $J = 8.5$ Hz, 1H), 5.92 (m, 1H), 5.83 – 5.69 (m, 1H), 4.77 (s, 2H), 4.69 (d, $J = 5.5$ Hz, 2H), 4.09 (d, $J = 5.1$ Hz, 2H), 3.99 (s, 3H), 3.82 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.12, 164.02, 159.39, 159.32, 155.53, 144.98, 142.26, 137.40, 136.09, 129.34, 128.98, 128.69, 128.18, 127.79, 127.56, 127.43, 116.91, 115.71, 110.99, 67.97, 67.31, 54.94, 53.75. HRMS (ESI) calcd for C$_{26}$H$_{26}$N$_2$O$_6$ [M+H]$^+$: 463.1882, Found: 463.1853.
(E)-4-(N-benzyl-2-hydroxy-4-(naphthalen-2-yl)benzamido)but-2-en-1-yl methyl carbonate (1u)

Yellow oil, 0.87 g, 90% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (m, 3H), 7.64 – 7.31 (m, 12H), 7.22 (s, 1H), 6.96 (d, $J = 7.7$ Hz, 1H), 5.96 (m, 1H), 5.82 (m, 1H), 4.84 (s, 2H), 4.72 (d, $J = 4.5$ Hz, 2H), 4.17 (d, $J = 3.4$ Hz, 2H), 3.84 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.30, 158.96, 155.56, 145.69, 138.98, 136.22, 133.77, 131.17, 129.49, 128.99, 128.33, 128.19, 127.90, 127.80, 127.56, 127.37, 126.71, 126.25, 125.93, 125.78, 125.31, 120.65, 119.63, 116.15, 67.34, 55.41, 54.94. HRMS (ESI) calcd for C$_{30}$H$_{27}$NO$_5$ [M+H]$^+$: 482.1917, Found: 482.1953.

(E)-4-(2-hydroxy-N-(4-methoxybenzyl)benzamido)but-2-en-1-yl methyl carbonate (1v)

Yellow oil, 0.74 g, 96% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.28 (m, 2H), 7.23 (d, $J = 8.1$ Hz, 2H), 7.03 (d, $J = 8.2$ Hz, 1H), 6.92 (d, $J = 8.4$ Hz, 2H), 6.81 (t, $J = 7.4$ Hz, 1H), 5.80 (m, 2H), 4.69 (s, 2H), 4.52 (d, $J = 4.2$ Hz, 2H), 4.12 (d, $J = 5.3$ Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.20, 171.15, 159.28, 158.78, 155.51, 132.74, 129.65, 128.81, 127.91, 127.62, 127.21, 118.73, 118.12, 114.36, 63.01, 60.40, 55.31, 54.87. HRMS (ESI) calcd for C$_{21}$H$_{23}$NO$_6$ [M+H]$^+$: 386.1598, Found: 386.1591.
(Z)-4-(2-hydroxy-N-(4-methoxybenzyl)benzamido)but-2-en-1-yl methyl carbonate ((Z)-1v)

Yellow oil, 0.73 g, 95% yield; $^1$H NMR (400 MHz, ) δ 7.36 – 7.27 (m, 2H), 7.23 (d, $J = 7.9$ Hz, 2H), 7.03 (d, $J = 8.2$ Hz, 1H), 6.92 (d, $J = 8.1$ Hz, 2H), 6.81 (t, $J = 7.5$ Hz, 1H), 5.80 (m, 2H), 4.69 (s, 2H), 4.52 (d, $J = 4.3$ Hz, 2H), 4.14 – 4.10 (m, 2H), 3.83 (s, 3H), 3.79 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.20, 159.28, 158.78, 155.51, 132.74, 129.65, 128.81, 127.91, 127.62, 127.21, 118.73, 118.12, 117.57, 114.36, 67.32, 63.01, 60.40, 55.31, 54.87.

3.2 General Procedure for the Allylic Etherification of 1

In a dry Schlenk tube filled with argon, [Ir(cod)Cl]$_2$ (2.7 mg, 0.004 mmol, 2 mol %), phosphoramidite ligand L7 (4.1 mg, 0.008 mmol, 4 mol %), and $n$-propylamine (0.5 mL) were dissolved in THF (1.0 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed in vacuum to give a yellow solid. In this tube, allylic carbonates 1 (0.2 mmol), DBU (61 mg, 0.4 mmol, 200 mol %) and THF (2.0 mL) were added and stirred at 25 °C until the reaction was complete. Then the solvent was evaporated and the residue was purified by silica gel column chromatography using
petroleum/EtOAc as the eluent to give the desired products. (2v is prepared from (Z)-1v in the same way.)

(R)-4-Benzyl-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2a)

\[
\text{R}_f = 0.50 \text{ (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 53.6 mg, 96% yield; 93% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 80/20, } \nu = 1.0 \text{ mL•min}^{-1}, T = 25 \text{ °C, } \lambda = 254 \text{ nm, } t_R \text{ (minor) = 12.051 min, } t_R \text{ (major) = 12.358 min]; } [\alpha]_{D}^{25} = +4.3^\circ \text{ (c = 0.70, CH}_2\text{Cl}_2). \text{ }^1H \text{ NMR (400 MHz, CDCl}_3 \text{) } \delta 7.87 \text{ (dd, } J = 7.7, 1.7 \text{ Hz, 1H), 7.47 – 7.42 (m, 1H), 7.40 – 7.35 (m, 4H), 7.35 – 7.29 (m, 1H), 7.23 (td, } J = 7.6, 1.1 \text{ Hz, 1H), 7.03 (dd, } J = 8.1, 0.8 \text{ Hz, 1H), 5.83 (ddd, } J = 17.1, 10.6, 6.3 \text{ Hz, 1H), 5.35 (m, 1H), 5.26 (m, 1H), 5.16 (d, } J = 14.8 \text{ Hz, 1H), 4.77 – 4.69 (m, 1H), 4.58 (d, } J = 14.8 \text{ Hz, 1H), 3.40 (m, 2H). } ^{13}C \text{ NMR (101 MHz, CDCl}_3 \text{) } \delta 168.84, 152.78, 137.01, 134.19, 132.74, 130.76, 128.79, 128.24, 127.75, 124.11, 122.57, 118.24, 84.10, 51.01, 49.60. \text{ HRMS (ESI) calcd for } \text{C}_{18}\text{H}_{17}\text{NO}_2 \text{ [M+H]}^+: 280.1341, \text{ Found: 280.1328.}
\]

(R)-4-Benzyl-8-methyl-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2b)

\[
\text{R}_f = 0.50 \text{ (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 55.1 mg, 94% yield; 92% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 80/20, } \nu = 1.0 \text{ mL•min}^{-1}, T = 25 \text{ °C, } \lambda = 254 \text{ nm, } t_R \text{ (minor) = 13.913 min, } t_R \text{ (major) =}
\]

S16
15.770 min]; \([\alpha]_D^{25} = +62.6^\circ\) (c = 0.70, CH\(_2\)Cl\(_2\)). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.75 (d, \(J = 7.9\) Hz, 1H), 7.43 – 7.31 (m, 5H), 7.09 – 7.00 (m, 1H), 6.88 – 6.78 (m, 1H), 5.82 (ddd, \(J = 17.0, 10.6, 6.3\) Hz, 1H), 5.33 (m, 1H), 5.25 (m, 1H), 5.14 (d, \(J = 14.8\) Hz, 1H), 4.71 (m, 1H), 4.57 (d, \(J = 14.8\) Hz, 1H), 3.39 (m, 2H), 2.38 (s, 3H).

\(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 168.91, 152.78, 143.58, 137.11, 134.34, 130.72, 128.76, 128.24, 127.69, 125.05, 124.88, 122.84, 118.09, 83.93, 51.01, 49.75, 25.37, 21.34. HRMS (ESI) calcd for C\(_{19}\)H\(_{19}\)NO\(_2\) [M+H]\(^+\): 294.1498, Found: 294.1483.

(R)-4-Benzyl-7-methyl-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2c)

![Chemical Structure](image.png)

R\(_f\) = 0.50 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 58.1 mg, 99% yield; 96% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), \(n\)-hexane/2-propanol = 93/7, \(v = 1.0\) mL•min\(^{-1}\), \(T = 25\) °C, \(\lambda = 254\) nm, \(t_R\) (minor) = 19.212 min, \(t_R\) (major) = 18.091 min]; \([\alpha]_D^{25} = +63.7^\circ\) (c = 0.70, CH\(_2\)Cl\(_2\)). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65 (s, 1H), 7.49 – 7.31 (m, 5H), 7.24 (d, \(J = 8.0\) Hz, 1H), 6.93 (d, \(J = 8.2\) Hz, 1H), 5.83 (ddd, \(J = 17.0, 10.2, 6.7\) Hz, 1H), 5.34 (d, \(J = 17.2\) Hz, 1H), 5.25 (d, \(J = 10.6\) Hz, 1H), 5.13 (d, \(J = 14.8\) Hz, 1H), 4.76 – 4.66 (m, 1H), 4.59 (d, \(J = 14.8\) Hz, 1H), 3.37 (m, 2H), 2.38 (s, 3H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 169.09, 150.50, 137.11, 134.33, 133.81, 133.38, 130.81, 128.77, 128.21, 128.05, 127.70, 122.37, 118.13, 83.90, 50.96, 49.63, 20.62. HRMS (ESI) calcd for C\(_{19}\)H\(_{19}\)NO\(_2\) [M+H]\(^+\): 294.1498, Found: 294.1483.

(R)-4-Benzyl-6-methyl-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2d)
$R_f = 0.50$ (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 55.1 mg, 94% yield; 99% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 90/10, $v = 1.0 \text{mL} \cdot \text{min}^{-1}$, $T = 25 \, ^\circ\text{C}$, $\lambda = 254 \, \text{nm}$, $t_R$ (minor) = 13.197 min, $t_R$ (major) = 11.893 min]; $[\alpha]_D^{25} = +47.7^\circ$ (c = 0.70, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (m, 6H), 7.09 (dd, $J = 7.3$, 2.9 Hz, 1H), 6.87 (dd, $J = 7.7$, 2.9 Hz, 1H), 5.93 – 5.73 (m, 1H), 5.30 (m, 2H), 5.13 (m, 1H), 4.72 – 4.58 (m, 2H), 3.39 – 3.24 (m, 2H), 2.55 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.13, 152.11, 139.56, 137.44, 134.26, 130.92, 128.77, 128.00, 127.66, 127.36, 120.40, 118.37, 83.38, 50.07, 48.95, 20.29. HRMS (ESI) calcd for C$_{19}$H$_{19}$NO$_2$ [M+H]$^+$: 294.1498, Found: 294.1483.

(R)-4-Benzyl-9-methoxy-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2e)

$R_f = 0.40$ (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 59.4 mg, 96% yield; 99% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 90/10, $v = 1.0 \text{mL} \cdot \text{min}^{-1}$, $T = 25 \, ^\circ\text{C}$, $\lambda = 211 \, \text{nm}$, $t_R$ (minor) = 24.718 min, $t_R$ (major) = 23.458 min]; $[\alpha]_D^{25} = +50.0^\circ$ (c = 0.80, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (t, $J = 10.3$ Hz, 6H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.07 (d, $J = 8.1$ Hz, 1H), 5.85 (ddd, $J = 17.1$, 10.6, 6.6 Hz, 1H), 5.35 (d, $J = 16.9$ Hz, 1H), 5.21 (m, 2H), 4.86 – 4.72 (m, 1H), 4.56 (d, $J = 14.7$ Hz, 1H), 3.88 (s, 3H), 3.37 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.81, 152.39, 141.96, 137.09, 134.57, 130.23, 128.77,
128.19, 127.71, 124.47, 121.71, 118.00, 114.96, 84.72, 56.22, 50.92, 49.71. 

(R)-4-Benzyl-8-methoxy-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2f)

Rᵥ = 0.40 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 60.0 mg, 97% yield; 91% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 85/15, ν = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, tᵣ (minor) = 15.317 min, tᵣ (major) = 16.151 min]; [α]D²⁵ = +60.5° (c = 0.80, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.7 Hz, 1H), 7.42 – 7.31 (m, 5H), 6.76 (dd, J = 8.8, 2.2 Hz, 1H), 6.54 (d, J = 2.1 Hz, 1H), 5.83 (ddd, J = 17.0, 10.5, 6.3 Hz, 1H), 5.33 (d, J = 17.2 Hz, 1H), 5.25 (d, J = 10.5 Hz, 1H), 5.14 (d, J = 14.7 Hz, 1H), 4.72 (m, 1H), 4.55 (d, J = 14.8 Hz, 1H), 3.84 (s, 3H), 3.48 – 3.30 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 168.64, 163.33, 154.60, 137.16, 134.30, 132.40, 128.76, 128.27, 127.69, 119.92, 118.15, 110.21, 106.99, 84.00, 55.52, 51.14, 49.92. HRMS (ESI) calcd for C₁₉H₁₉NO₃ [M+H]⁺: 310.1447, Found: 310.1432.

(R)-4-Benzyl-7-methoxy-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2g)

Rᵥ = 0.50 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 59.4 mg, 96% yield; 94% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 90/10, ν =
1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 20.603 min, t_R (major) = 19.327 min; [α]_D = +61.8° (c = 0.80, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.32 (m, 6H), 6.98 (m, 2H), 5.82 (ddd, J = 17.1, 10.6, 6.4 Hz, 1H), 5.33 (m, 1H), 5.25 (m, 1.1 Hz, 1H), 5.14 (d, J = 14.8 Hz, 1H), 4.68 (m, 1H), 4.59 (d, J = 14.8 Hz, 1H), 3.85 (s, 3H), 3.37 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 168.86, 156.15, 146.33, 137.06, 134.28, 129.16, 128.78, 128.20, 127.74, 123.69, 119.49, 118.21, 113.68, 83.92, 55.81, 51.03, 49.63. HRMS (ESI) calcd for C₁₉H₁₉NO₃ [M+H]+: 310.1447, Found: 310.1432.

(R)-4-Benzyl-6-methoxy-2-vinyl-3,4-dihydrobenzof[1,4]oxazepin-5(2H)-one (2h)

R_f = 0.40 (petroleum/EtOAc = 2:1, v/v); yellow oil, 53.8 mg, 87% yield; 96% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 75/25, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 17.409 min, t_R (major) = 14.163 min]; [α]_D = +52.9° (c = 0.80, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.37 (m, 6H), 6.82 (d, J = 8.4 Hz, 1H), 6.65 (d, J = 8.1 Hz, 1H), 5.85 – 5.72 (m, 1H), 5.25 (m, 3H), 4.56 (d, J = 14.9 Hz, 2H), 3.94 (s, 3H), 3.42 (m, 1H), 3.28 (m, 1H). ¹³C NMR (101 MHz, ) δ 166.01, 158.76, 152.92, 137.38, 134.21, 131.83, 128.73, 128.31, 127.66, 124.46, 123.97, 119.11, 118.53, 118.36, 115.34, 108.26, 83.56, 56.33, 49.91, 48.90. HRMS (ESI) calcd for C₁₉H₁₉NO₃ [M+H]+: 310.1447, Found: 310.1433.

(R)-4-Benzyl-8-fluoro-2-vinyl-3,4-dihydrobenzof[1,4]oxazepin-5(2H)-one (2i)
\( R_f = 0.60 \) (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 58.8 mg, 99% yield; 91% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), \( n \)-hexane/2-propanol = 85/15, \( v = 1.0 \text{ mL} \cdot \text{min}^{-1}, T = 25 \text{ °C}, \lambda = 254 \text{ nm}, t_R \text{ (minor)} = 9.738 \text{ min}, t_R \text{ (major)} = 9.109 \text{ min}] ; [\alpha]_D^{25} = +63.1^\circ \text{ (c = 0.70, CH}_2\text{Cl}_2). \) 

\( ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.90 \text{ (t, } J = 7.6 \text{ Hz, 1H}), 7.46 - 7.31 \text{ (m, 5H), 6.93 (t, } J = 8.2 \text{ Hz, 1H), 6.75 (d, } J = 9.5 \text{ Hz, 1H), 5.81 (ddd, } J = 17.0, 10.4, 6.3 \text{ Hz, 1H), 5.30 (m, 2H), 5.15 (d, } J = 14.8 \text{ Hz, 1H), 4.73 (s, 1H), 4.55 (d, } J = 14.8 \text{ Hz, 1H), 3.53 - 3.32 \text{ (m, 2H).} \) 

\( ^{13}\text{C NMR} \ (101 \text{ MHz, CDCl}_3) \delta 167.87, 165.22 \text{ (d, } J = 251.0 \text{ Hz), 154.57 (d, } J = 12.0 \text{ Hz), 136.84, 133.81, 132.88 (d, } J = 10.4 \text{ Hz), 128.83, 128.29, 127.84, 123.88 (d, } J = 3.2 \text{ Hz), 118.48, 111.45, 111.23, 109.67, 109.44, 84.29, 51.19, 49.66.} \) 

\( ^{19}\text{F NMR} \ (376 \text{ MHz, CDCl}_3) \delta -106.79. \) 

HRMS (ESI) calcd for C\(_{18}\)H\(_{16}\)FNO\(_2\) [M+H]\(^+\): 298.1246, Found: 298.1234.

\((R)\)-4-Benzyl-7-fluoro-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2\(H\)) -one (\textit{2j})

\( R_f = 0.60 \) (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 55.3 mg, 93% yield; 91% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), \( n \)-hexane/2-propanol = 95/5, \( v = 1.0 \text{ mL} \cdot \text{min}^{-1}, T = 25 \text{ °C}, \lambda = 254 \text{ nm}, t_R \text{ (minor)} = 19.535 \text{ min}, t_R \text{ (major)} = 18.155 \text{ min}]; [\alpha]_D^{25} = +62.3^\circ \text{ (c = 0.70, CH}_2\text{Cl}_2). \) 

\( ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.54 \text{ (dd, } J = 8.5, 3.1 \text{ Hz, 1H), 7.43 - 7.30 \text{ (m, 5H), 7.13 (td, } J = 8.3, 3.0 \text{ Hz, 1H), 7.00 (dd, } J = 8.8, 4.6 \text{ Hz, 1H), 5.81 (ddd, } J = 17.0, 10.5, 6.3 \text{ Hz, 1H), 5.31 (m,} \)
2H), 5.14 (d, $J = 14.8$ Hz, 1H), 4.70 (m, 1H), 4.56 (d, $J = 14.8$ Hz, 1H), 3.50 – 3.28 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.69, 159.03 (d, $J = 242.0$ Hz), 148.71 (d, $J = 2.5$ Hz), 136.77, 133.89, 129.77 (d, $J = 7.4$ Hz), 128.84, 128.25, 127.86, 124.05 (d, $J = 8.0$ Hz), 119.59, 119.36, 118.49, 117.02, 116.77, 84.05, 51.10, 49.47. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -118.43. HRMS (ESI) calced for C$_{18}$H$_{16}$FNO$_2$ [M+H]$^+$: 298.1246, Found: 298.1233.

(R)-4-Benzyl-8-chloro-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2k)

\[
\text{R}_f = 0.60 \text{ (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 60.1 mg, 96\% yield; 90\% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 85/15, v = 1.0 mL•min$^{-1}$, T = 25 °C, $\lambda$ = 254 nm, t$_R$ (minor) = 11.135 min, t$_R$ (major) = 10.491 min]; [a]$_D^{25}$ = -74.2° (c = 0.80, CH$_2$Cl$_2$).}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 8.4$ Hz, 1H), 7.45 – 7.31 (m, 5H), 7.20 (d, $J = 8.3$ Hz, 1H), 7.05 (s, 1H), 5.80 (ddd, $J = 17.0$, 10.5, 6.3 Hz, 1H), 5.31 (m, 2H), 5.14 (d, $J = 14.7$ Hz, 1H), 4.73 (m, 1H), 4.55 (d, $J = 14.8$ Hz, 1H), 3.41 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.83, 153.58, 138.16, 136.74, 133.73, 132.11, 128.85, 128.31, 127.88, 126.26, 124.30, 122.67, 118.58, 84.32, 51.18, 49.58. HRMS (ESI) calcd for C$_{18}$H$_{16}$ClNO$_2$ [M+H]$^+$: 314.0951, Found: 314.0936.

(R)-4-Benzyl-7-chloro-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2l)
$R_f = 0.60$ (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 60.7 mg, 97% yield; 92% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 93/7, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ °C}$, $\lambda = 254 \text{ nm}$, $t_R$ (minor) = 15.568 min, $t_R$ (major) = 14.780 min]; $[\alpha]^D_{25} = -76.9^\circ$ (c = 0.80, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (s, 1H), 7.36 (s, 6H), 6.97 (d, $J = 8.4$ Hz, 1H), 5.90 – 5.71 (m, 1H), 5.31 (m, 2H), 5.13 (d, $J = 14.4$ Hz, 1H), 4.72 (d, $J = 4.7$ Hz, 1H), 4.57 (d, $J = 14.5$ Hz, 1H), 3.55 – 3.25 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.48, 151.37, 136.69, 133.79, 132.62, 130.55, 129.41, 128.86, 128.27, 127.89, 124.01, 118.55, 84.11, 51.15, 49.46. HRMS (ESI) calcd for C$_{18}$H$_{16}$ClNO$_2$ [M+H]$^+$: 314.0951, Found: 314.0936.

**(R)-4-Benzyl-7-bromo-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2m)**

$R_f = 0.60$ (petroleum/EtOAc = 2 : 1, v/v); brown oil, 60.7 mg, 85% yield; 91% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 95/5, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ °C}$, $\lambda = 254 \text{ nm}$, $t_R$ (minor) = 20.457 min, $t_R$ (major) = 19.384 min]; $[\alpha]^D_{25} = -67.8^\circ$ (c = 0.90, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J = 2.6$ Hz, 1H), 7.53 (dd, $J = 8.5$, 2.5 Hz, 1H), 7.41 – 7.32 (m, 5H), 6.91 (d, $J = 8.6$ Hz, 1H), 5.79 (ddd, $J = 17.0$, 10.6, 6.3 Hz, 1H), 5.30 (m, 2H), 5.12 (d, $J = 14.7$ Hz, 1H), 4.72 (m, 1H), 4.57 (d, $J = 14.8$ Hz, 1H), 3.47 – 3.29 (m, 2H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.33, 151.92, 136.68, 135.57, 133.78, 133.53, 129.71, 128.86, 128.27, 127.89, 124.35, 118.54, 116.75, 84.09, 51.17, 49.46. HRMS (ESI) calcd for C$_{18}$H$_{16}$BrNO$_2$ [M+H]$^+$: 358.0446, Found: 358.0432.

(R)-4-Benzyl-8-nitro-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2n)

$\text{R_f} = 0.40$ (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 58.3 mg, 90% yield; 84% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), $n$-hexane/2-propanol = 85/15, $\nu$ = 1.0 mL•min$^{-1}$, $T$ = 25 °C, $\lambda$ = 254 nm, $t_R$ (minor) = 22.654 min, $t_R$ (major) = 19.424 min]; $[\alpha]_D^{25} = +21.3^\circ$ (c = 0.50, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (s, 2H), 7.88 (s, 1H), 7.50 – 7.30 (m, 6H), 5.81 (ddd, $J$ = 16.9, 10.5, 6.2 Hz, 1H), 5.40 – 5.31 (m, 2H), 5.17 (d, $J$ = 14.7 Hz, 1H), 4.80 (m, 1H), 4.57 (d, $J$ = 14.7 Hz, 1H), 3.48 – 3.40 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.68, 153.38, 150.48, 136.27, 133.54, 133.14, 132.27, 128.97, 128.37, 128.11, 119.12, 118.47, 117.99, 84.67, 51.32, 49.28. HRMS (ESI) calcd for C$_{18}$H$_{16}$N$_2$O$_4$ [M+H]$^+$: 325.1192, Found: 325.1180.

(R)-4-Benzyl-8-(trifluoromethyl)-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2o)
R_f = 0.40 (petroleum/EtOAc = 2 : 1, v/v); pale yellow oil, 57.6 mg, 83% yield; 80% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 90/10, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 12.495 min, t_R (major) = 11.473 min]; [α]_D^{25} = -49.1° (c = 0.60, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 7.7 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.43 – 7.28 (m, 6H), 5.91 – 5.74 (m, 1H), 5.33 (m, 2H), 5.17 (d, J = 14.8 Hz, 1H), 4.84 – 4.71 (m, 1H), 4.57 (d, J = 14.6 Hz, 1H), 3.51 – 3.32 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 167.43, 153.05, 136.54, 133.54, 131.88, 131.02, 128.90, 128.32, 127.98, 120.50 (d, J = 3.6 Hz), 119.77 (d, J = 3.7 Hz), 118.77, 84.46, 51.22, 49.42. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.08. HRMS (ESI) calcd for C₁₉H₁₆F₃NO₂ [M+H]^+: 348.1216, Found: 348.1200.

(R)-4-Benzyl-2-vinyl-3,4-dihyronaphtho[2,3-f][1,4]oxazepin-5(2H)-one (2p)

R_f = 0.60 (petroleum/EtOAc = 2 : 1, v/v); pale yellow oil, 61.2 mg, 93% yield; 91% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 85/15, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 32.663 min, t_R (major) = 34.811 min]; [α]_D^{25} = -19.6° (c = 0.50, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 8.39 (s, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.38 (dd, J = 16.3, 7.7 Hz, 5H), 5.91 (ddd, J = 17.2, 10.5, 6.6 Hz, 1H), 5.40 (d, J = 17.3 Hz, 1H), 5.31 (d, J = 10.6 Hz, 1H), 5.20 (d, J = 14.8 Hz, 1H), 4.74 (m, 1H), 4.65 (d, J = 14.8 Hz, 1H), 3.50 – 3.33 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 168.88, 149.30, 137.11, 135.66, 134.15, 131.45, 130.41, 129.49, 128.82, 128.23, 127.82, 126.92, 125.63, 119.46, 118.50, 83.42,

S25
50.99, 49.42. HRMS (ESI) calcd for C_{22}H_{19}NO_{2} [M+H]^+: 330.1502, Found: 330.1482.

**(R)-4-Benzyl-2-vinyl-3,4-dihydropyrido[4,3-f][1,4]oxazepin-5(2H)-one (2q)**

\[
\text{HRMS (ESI) calcd for C}_{17}\text{H}_{16}\text{N}_{2}\text{O}_{2}[M+H]^+: 281.1292, \text{Found: 281.1280.}
\]

**1H NMR (400 MHz, CDCl}_3) \delta 8.47 (s, 2H), 7.83 (d, J = 2.7 Hz, 1H), 7.50 – 7.33 (m, 5H), 5.79 (m, 1H), 5.41 – 5.26 (m, 2H), 5.17 (d, J = 14.2 Hz, 1H), 4.80 (s, 1H), 4.54 (d, J = 14.5 Hz, 1H), 3.45 (s, 2H).**

**13C NMR (101 MHz, CDCl}_3) \delta 166.50, 148.49, 144.77, 144.44, 136.17, 133.29, 132.64, 128.95, 128.40, 128.09, 123.85, 118.75, 84.14, 51.47, 49.67.**

**(R)-4-Benzyl-8-(thiophen-3-yl)-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2r)**

\[
\text{HRMS (ESI) calcd for C}_{17}\text{H}_{16}\text{N}_{2}\text{O}_{2}[M+H]^+: 281.1292, \text{Found: 281.1280.}
\]

**1H NMR (400 MHz, CDCl}_3) \delta 8.47 (s, 2H), 7.83 (d, J = 2.7 Hz, 1H), 7.50 – 7.33 (m, 5H), 5.79 (m, 1H), 5.41 – 5.26 (m, 2H), 5.17 (d, J = 14.2 Hz, 1H), 4.80 (s, 1H), 4.54 (d, J = 14.5 Hz, 1H), 3.45 (s, 2H).**

\[\text{[α]D}^{25} = -5.7° \text{ (c = 0.60, CH}_2\text{Cl}_2).\]
7.91 (d, \( J = 8.0 \) Hz, 1H), 7.56 (s, 1H), 7.51 – 7.27 (m, 9H), 5.86 (ddd, \( J = 17.0 \), 10.1, 6.7 Hz, 1H), 5.37 (d, \( J = 17.2 \) Hz, 1H), 5.28 (d, \( J = 10.5 \) Hz, 1H), 5.18 (d, \( J = 14.7 \) Hz, 1H), 4.76 (s, 1H), 3.46 (m, 2H).  \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 168.57, 153.35, 140.84, 140.31, 137.02, 134.23, 131.54, 128.81, 128.30, 127.77, 126.62, 126.25, 126.14, 121.89, 121.69, 120.03, 118.32, 84.08, 51.14, 49.76. HRMS (ESI) calcd for C\(_{22}\)H\(_{19}\)NO\(_3\)S \([\text{M+H}]^+\): 362.1223, Found: 362.1205.

\((R)-4\)-Benzyl-8-(furan-2-yl)-2-vinyl-3,4-dihydrobenzo[\(f\)]1,4]oxazepin-5(2\(H\))-one (2s)

![Chemical structure](image)

\( R_f = 0.60 \) (petroleum/EtOAc = 2 : 1, v/v); pale yellow oil, 67.0 mg, 97% yield; 92% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), \( n \)-hexane/2-propanol = 85/15, \( v = 1.0 \) mL\cdot\text{min}^{-1}, \( T = 25 \) °C, \( \lambda = 254 \) nm, \( t_R \) (minor) = 14.863 min, \( t_R \) (major) = 15.557 min]; \([\alpha]_D^{25} = -8.4^\circ \) (c = 0.60, CH\(_2\)Cl\(_2\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.89 (d, \( J = 8.1 \) Hz, 1H), 7.52 (d, \( J = 6.5 \) Hz, 2H), 7.45 – 7.28 (m, 6H), 6.77 (s, 1H), 6.52 (s, 1H), 5.86 (ddd, \( J = 17.1 \), 10.5, 6.4 Hz, 1H), 5.36 (d, \( J = 17.2 \) Hz, 1H), 5.28 (d, \( J = 10.6 \) Hz, 1H), 5.16 (d, \( J = 14.8 \) Hz, 1H), 4.75 (s, 1H), 4.58 (d, \( J = 14.8 \) Hz, 1H), 3.55 – 3.33 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 168.50, 153.35, 152.60, 142.96, 137.01, 135.10, 134.20, 131.47, 128.80, 128.30, 127.77, 126.41, 119.23, 118.31, 117.35, 111.94, 106.99, 84.06, 51.11, 49.72. HRMS (ESI) calcd for C\(_{22}\)H\(_{19}\)NO\(_3\)S \([\text{M+H}]^+\): 346.1451, Found: 346.1433.

\((R)-4\)-Benzyl-8-(6-methoxypyridin-3-yl)-2-vinyl-3,4-dihydrobenzo[\(f\)]1,4]oxazepin-5(2\(H\))-one (2t)

S27
$R_f = 0.60$ (petroleum/EtOAc = 2 : 1, v/v); pale yellow oil, 74.1 mg, 96% yield; 92% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 85/15, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \degree C$, $\lambda = 254 \text{ nm}$, $t_R$ (minor) = 21.300 min, $t_R$ (major) = 27.712 min]; $[\alpha]_D^{25} = -6.3^{\circ}$ (c = 0.60, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.43 (d, $J = 2.4$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.82 (dd, $J = 8.6, 2.5$ Hz, 1H), 7.42 – 7.31 (m, 6H), 7.20 (d, $J = 1.5$ Hz, 1H), 6.85 (d, $J = 8.6$ Hz, 1H), 5.85 (ddd, $J = 17.0, 10.6, 6.3$ Hz, 1H), 5.36 (d, $J = 17.2$ Hz, 1H), 5.27 (d, $J = 10.6$ Hz, 1H), 5.18 (d, $J = 14.8$ Hz, 1H), 4.77 (m, 1H), 4.58 (d, $J = 14.8$ Hz, 1H), 4.01 (s, 3H), 3.45 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.48, 164.07, 153.39, 145.09, 142.51, 137.39, 136.95, 134.10, 131.72, 128.83, 128.53, 128.28, 127.80, 126.51, 122.01, 120.28, 118.40, 111.05, 84.13, 53.74, 51.14, 49.71. HRMS (ESI) calcd for C$_{24}$H$_{22}$N$_2$O$_3$ [M+H]$^+$: 387.1719, Found: 387.1698.

(R)-4-Benzyl-8-(naphthalen-2-yl)-2-vinyl-3,4-dihydrobenzof[f][1,4]oxazepin-5(2H)-one (2u)

$R_f = 0.60$ (petroleum/EtOAc = 2 : 1, v/v); pale yellow oil, 76.2 mg, 94% yield; 94% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 90/10, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \degree C$, $\lambda = 254 \text{ nm}$, $t_R$ (minor) = 42.743 min, $t_R$ (major) = 38.050 min]; $[\alpha]_D^{25} = +22.1^{\circ}$ (c = 0.70, CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J = 7.8$ Hz, 1H), 7.93 (t, $J = 9.5$ Hz, 3H), 7.60 – 7.35 (m, 10H), 7.22
(s, 1H), 5.94 – 5.80 (m, 1H), 5.37 (d, J = 17.2 Hz, 1H), 5.25 (m, 2H), 4.80 (s, 1H), 4.64 (d, J = 14.8 Hz, 1H), 3.54 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 168.74, 152.77, 145.69, 138.71, 137.05, 134.20, 133.81, 131.20, 130.83, 128.84, 128.38, 128.29, 127.81, 126.83, 126.70, 126.34, 125.97, 125.86, 125.68, 125.32, 124.01, 118.27, 84.11, 51.17, 49.82. HRMS (ESI) calcld for C\(_{24}\)H\(_{22}\)N\(_2\)O\(_3\) [M+H]+: 406.1807, Found: 406.1794.

\((R)-4-(4\text{-Methoxybenzyl})\text{-2-vinyl-3,4-dihydrobenzo}[f][1,4]oxazepin-5(2H)\text{-one (2v)}\)

![Chemical Structure](image)

**Trans-substrate:** \(R_f = 0.60\) (petroleum/EtOAc= 2 : 1, v/v); pale yellow oil, 57.5 mg, 93% yield; 90% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 95/5, \(v = 1.0\) mL\(\cdot\)min\(^{-1}\), t = 25 °C, \(\lambda = 254\) nm, \(t_R\) (minor) = 35.879 min, \(t_R\) (major) = 33.676 min]; \([\alpha]_D^{25} = +4.5^\circ\) (c = 0.50, CH\(_2\)Cl\(_2\)). **Cis-substrate:** \(R_f = 0.60\) (petroleum/EtOAc= 2 : 1, v/v); pale yellow oil, 58.7 mg, 95% yield; -73% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 95/5, \(v = 1.0\) mL\(\cdot\)min\(^{-1}\), t = 25 °C, \(\lambda = 254\) nm, \(t_R\) (minor) = 34.931 min, \(t_R\) (major) = 36.551 min]; \([\alpha]_D^{25} = -4.1^\circ\) (c = 0.50, CH\(_2\)Cl\(_2\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 7.6\) Hz, 1H), 7.44 (t, \(J = 7.6\) Hz, 1H), 7.31 (d, \(J = 8.4\) Hz, 2H), 7.22 (t, \(J = 7.4\) Hz, 1H), 7.03 (d, \(J = 8.1\) Hz, 1H), 6.91 (d, \(J = 8.0\) Hz, 2H), 5.82 (ddd, \(J = 17.0, 10.2, 6.6\) Hz, 1H), 5.35 (d, \(J = 17.3\) Hz, 1H), 5.26 (d, \(J = 10.6\) Hz, 1H), 5.12 (d, \(J = 14.6\) Hz, 1H), 4.70 (s, 1H), 4.49 (d, \(J = 14.6\) Hz, 1H), 3.83 (s, 3H), 3.47 – 3.30 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 168.72, 159.25, 152.76, 134.28, 132.66, 130.76, 129.67, 129.12, 128.36, 124.06, 122.54, 118.15, 114.17, 

S29
55.31, 50.45, 49.40. HRMS (ESI) calcd for C_{19}H_{19}NO_3 [M+H]⁺: 310.1393, Found: 310.1433.

### 3.3 Gram-scale Reaction

![Reaction Scheme](image)

Representative Procedure: in a dry Schlenk tube (50.0 mL) filled with argon, [Ir(cod)Cl]_2 (37.8 mg, 0.056 mmol, 2 mol %), ligand L7 (57.6 mg, 0.113 mmol, 4 mol %), and n-propylamine (5.0 mL) were dissolved in THF (10.0 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed in vacuum to give a yellow solid. In glove box, substrate (1 g, 2.82 mmol), DBU (0.857 g, 5.64 mmol, 200 mol %) and solvent (20.0 mL) were added into the above tube and stirred at 25 °C until the reaction was complete. Then the solvent was evaporated and the residue was purified by silica gel column chromatography using petroleum/EtOAc as the eluent to give the desired product (92% yield, 91% ee).

### 3.4 Procedure for the Synthesis of 3v

![Reaction Scheme](image)

30.9 mg, 90% ee

16.8 mg, 89% yield, 89% ee

S30
In a dry Schlenk tube filled with argon, 2v (30.9 mg, 0.1 mmol) was dissolved in excessive TFA (10 mL). The reaction mixture was heated at 60 °C for 1 h. Then the crude reaction mixture was diluted with DCM (10 mL) and washed with saturated sodium bicarbonate solution (10 mL x 3) and brine (10 mL x 3). The combined organic layers were dried over Na₂SO₄. Afterwards, the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum/EtOAc = 1 : 1) to afford the desired products 3v (89% yield, 89% ee).

(R)-2-Vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (3v)

\[
\begin{align*}
\text{R}_f &= 0.10 \text{ (petroleum/EtOAc = 2 : 1, v/v); black oil, 16.8 mg, 89\% yield; 89\% ee} \\
&\text{[Daicel Chiralcel IF-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 95/5, \( v = 1.0 \) mL·min}^{-1}, T = 25 ^\circ\text{C}, \lambda = 254 \text{ nm, } t_R \text{ (minor) = 31.262 min, } t_R \text{ (major) = 32.378 min]}; [\alpha]^{25}_D = +12.6^\circ \text{ (c = 0.30, CH}_2\text{Cl}_2). \ 
^1\text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.85 \text{ (d, } J = 7.6 \text{ Hz, 1H), 7.48 \text{ (t, } J = 7.6 \text{ Hz, 1H), 7.32} - 7.18 \text{ (m, 2H), 7.09 \text{ (d, } J = 8.1 \text{ Hz, 1H), 6.05} - 5.89 \text{ (m, 1H), 5.48 \text{ (d, } J = 17.1 \text{ Hz, 1H), 5.35 \text{ (d, } J = 10.6 \text{ Hz, 1H), 4.94 \text{ (s, 1H), 3.50 \text{ (d, } J = 14.5 \text{ Hz, 1H), 3.40} - 3.27 \text{ (m, 1H).} \ 
\text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3\text{) } \delta 171.17, 154.03, 134.26, 133.29, 130.86, 126.11, 123.77, 122.55, 118.39, 84.44, 44.63. HRMS (ESI) calcd for C}_{11}\text{H}_{11}\text{NO}_2 \text{ [M+H]}^+: 190.0863, \text{ Found: 190.0859.}
\end{align*}
\]
3.5 Procedure for the Synthesis of 3a

To a solution of 2a (139.6 mg, 0.5 mmol) in THF (10 mL) at 0 °C, LiAlH₄ (114 mg, 3 mmol) was added in three portions. The reaction mixture was stirred for 12 h at 50 °C. It was cooled back down to 0 °C and MeOH was added. Then the mixture was filtered through celite and the obtained solution was concentrated in vacuo. The crude residue was purified using column chromatography (eluent: petroleum ether/EtOAc = 2 : 1) to provide the desired product 3a (73% yield, 91% ee).

(R)-4-Benzyl-2-vinyl-2,3,4,5-tetrahydrobenzo[f][1,4]oxazepine (3a)

Rᵥ = 0.30 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 96.8 mg, 73% yield; 91% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), n-hexane/2-propanol = 99.5/0.5, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, tᵣ (minor) = 5.744 min, tᵣ (major) = 5.327 min]; [α]₂₅° = -9.5° (c = 0.40, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.24 (m, 6H), 7.14 – 7.00 (m, 3H), 5.94 (ddd, J = 16.0, 10.7, 5.2 Hz, 1H), 5.46 (m, 1H), 5.27 (m, 1H), 4.52 (d, J = 3.6 Hz, 1H), 4.08 (d, J = 14.2 Hz, 1H), 3.70 (m, 3H), 3.09 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 158.76, 138.43, 136.37, 131.97, 130.59, 128.99, 128.66, 128.40, 127.27, 123.58, 121.26, 116.03, 78.92, 62.41, 58.24, 56.97. HRMS (ESI) calcd for C₁₈H₁₉NO [M+H]⁺: 266.1539, Found: 266.1535.
3.6 Procedure for the Synthesis of 4a

A flame dried Schlenk tube was cooled to room temperature and filled with argon. To this flask 2a (111.7 mg, 0.4 mmol) and 9-BBN (0.5 M in THF, 2.4 mL, 1.2 mmol) were added. The reaction mixture was heated at 50 °C for 2 hours until the starting material was consumed completely (monitored by TLC). Then the reaction mixture was cooled to 0 °C, 3 M aqueous NaOH (0.8 mL) solution was added. After 5 min, 30% H$_2$O$_2$ (0.6 mL) was added by syringe. After stirring for an additional 3 hours at room temperature, saturated aqueous Na$_2$SO$_3$ solution was added, then the reaction mixture was extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, separated, dried over Na$_2$SO$_4$ and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EA = 1/1) to afford the desired product 4a (90% yield, 91% ee).

(R)-4-Benzyl-2-(2-hydroxyethyl)-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (4a)

R$_f$ = 0.10 (petroleum/EtOAc = 2 : 1, v/v); white solid, 107.1 mg, 90% yield; 91% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), n-hexane/2-propanol =
80/20, \( v = 1.0 \text{ mL} \cdot \text{min}^{-1}, T = 25 \degree \text{C}, \lambda = 254 \text{ nm}, t_R \text{ (minor)} = 13.672 \text{ min}, \)

\( t_R \text{ (major)} = 12.821 \text{ min} \}; [\alpha]_D^{25} = +3.7 \degree \text{ (c = 0.50, CH}_2\text{Cl}_2). \)

\( ^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.86 \text{ (d, } J = 7.6 \text{ Hz, } 1\text{H}), 7.49 - 7.31 \text{ (m, } 6\text{H}), 7.22 \text{ (t, } J = 7.4 \text{ Hz, } 1\text{H}), 6.98 \text{ (d, } J = 8.0 \text{ Hz, } 1\text{H}), 5.01 \text{ (d, } J = 14.8 \text{ Hz, } 1\text{H}), 4.72 \text{ (d, } J = 14.8 \text{ Hz, } 1\text{H}), 4.50 \text{ (s, } 1\text{H}), 3.85 \text{ (m, } 2\text{H}), 3.40 - 3.28 \text{ (m, } 2\text{H}), 1.91 \text{ (s, } 2\text{H).} \)

\( ^{13}\text{C NMR (101 MHz, CDCl}_3) \delta 168.94, 152.36, 137.07, 132.69, 130.84, 128.79, 128.45, 128.21, 127.74, 124.11, 122.55, 81.69, 59.41, 51.03, 50.03, 34.57. \text{ HRMS (ESI) calcd for C}_{18}\text{H}_{19}\text{NO}_3 [M+H]^+: 298.1438, Found: 298.1433.} \)
4. Copies of NMR Spectra

Figure 1. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1a

Figure 2. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1a
Figure 3. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) spectrum of 1b

Figure 4. \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) spectrum of 1b
Figure 5. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1c

Figure 6. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1c
Figure 7. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1d

Figure 8. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1d
Figure 9. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1e

Figure 10. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1e
Figure 11. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1f

Figure 12. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1f
Figure 13. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1g

Figure 14. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1g
Figure 15. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1h

Figure 16. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1h
Figure 17. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1i

Figure 18. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1i
Figure 19. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 1i

Figure 20. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1j
Figure 21. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1j

Figure 22. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 1j
Figure 23. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1k

Figure 24. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1k
Figure 25. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 11

Figure 26. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 11
Figure 27. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1m

Figure 28. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1m
Figure 29. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1n

Figure 30. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1n
Figure 31. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1o

Figure 32. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1o
Figure 33. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 1o

Figure 34. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1p
Figure 35. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1p

Figure 36. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1q
Figure 37. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1q

Figure 38. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1r
Figure 39. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1r

![Figure 39](image)

Figure 40. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1s

![Figure 40](image)
Figure 41. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1s

Figure 42. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1t
Figure 43. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1t

Figure 44. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1u
Figure 45. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1u

Figure 46. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of (E)-1v
Figure 47. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of (E)-1v

Figure 48. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of (Z)-1v
Figure 49. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of (Z)-1v

4-Benzyl-2-vinyl-3,4-dihydro-$2\lambda^3$-benzo[f][1,4]oxazepin-5(2H)-one (2a)

Figure 50. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2a
Figure 51. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2a

4-Benzyl-8-methyl-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2b)

Figure 52. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2b
Figure 53. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2b

4-Benzyl-7-methyl-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2c)

Figure 54. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2c
Figure 55. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2c

4-Benzyl-6-methyl-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2d)

Figure 56. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2d
Figure 57. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2d

4-Benzyl-9-methoxy-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2e)

Figure 58. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2e
Figure 59. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2e

4-Benzyl-8-methoxy-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2f)

Figure 60. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2f
Figure 61. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2f

4-Benzyl-7-methoxy-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2g)

Figure 62. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2g
4-Benzyl-6-methoxy-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2h)

Figure 63. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2g

Figure 64. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2h
Figure 65. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2h

4-Benzyl-8-fluoro-2-vinyl-3,4-dihydrobenzo[\(][1,4\)]oxazepin-5(2\(H\))\)-one (2i)

Figure 66. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2i
Figure 67. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2i

Figure 68. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 2i

S68
4-Benzyl-7-fluoro-2-vinyl-3,4-dihydrobenzo[\textit{f}][1,4]oxazepin-5(2\textit{H})-one (2j)

Figure 69. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2j

Figure 70. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2j
Figure 71. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 2j

4-Benzyl-8-chloro-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2k)

Figure 72. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2k
Figure 73. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2k

4-Benzyl-7-chloro-2-vinyl-3,4-dihydrobenzo[\textit{f}][1,4]oxazepin-5(2$H$)-one (2l)

Figure 74. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2l
Figure 75. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2l

4-Benzyl-7-bromo-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2m)

Figure 76. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2m
Figure 77. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2m

4-Benzyl-8-nitro-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2n)

Figure 78. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2n
Figure 79. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2n

![Chemical Structure with NMR Peaks](image)

4-Benzyl-8-(trifluoromethyl)-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2o)

Figure 80. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2o

![Chemical Structure with NMR Peaks](image)
Figure 81. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2o

Figure 82. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 2o
4-Benzyl-2-vinyl-3,4-dihyronaphtho[2,3-f][1,4]oxazepin-5(2H)-one (2p)

Figure 83. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2p

Figure 84. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2p
4-Benzyl-2-vinyl-3,4-dihydropyrido[4,3-f][1,4]oxazepin-5(2H)-one (2q)

Figure 85. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2q

Figure 86. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2q
4-Benzyl-8-(thiophen-3-yl)-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2r)

Figure 87. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2r

Figure 88. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2r
4-Benzyl-8-(furan-2-yl)-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2s)

Figure 89. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2s

Figure 90. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2s
4-Benzyl-8-(6-methoxypyridin-3-yl)-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2t)

Figure 91. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2t

Figure 92. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2t
4-Benzyl-8-(naphthalen-2-yl)-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2u)

Figure 93. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2u

Figure 94. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2u
4-(4-Methoxybenzyl)-2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (2v)

Figure 95. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2v

![Figure 95. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2v](image)

Figure 96. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2v

![Figure 96. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 2v](image)
2-vinyl-3,4-dihydrobenzo[f][1,4]oxazepin-5(2H)-one (3v)

Figure 97. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3v

Figure 98. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3v
4-Benzyl-2-vinyl-2,3,4,5-tetrahydrobenzo[f][1,4]oxazepane (3a)

Figure 99. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3a

Figure 100. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 3a
4-Benzyl-2-(2-hydroxyethyl)-3,4-dihydro-2λ3-benzo[f][1,4]oxazepin-5(2H)-one (4a)

Figure 101. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4a

Figure 102. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 4a
5. Copies of HPLC Chromatograms

Figure 103. HPLC spectra of 2a

2a (The top one is racemic, and the bottom one is chiral)
Figure 104. HPLC spectra of 2b

2b (The top one is racemic, and the bottom one is chiral)
Figure 105. HPLC spectra of 2c

2c (The top one is racemic, and the bottom one is chiral)
Figure 106. HPLC spectra of 2d

2d (The top one is racemic, and the bottom one is chiral)
Figure 107. HPLC spectra of 2e

2e (The top one is racemic, and the bottom one is chiral)
Figure 108. HPLC spectra of 2f

2f (The top one is racemic, and the bottom one is chiral)
Figure 109. HPLC spectra of 2g

![HPLC spectra of 2g]

2g (The top one is racemic, and the bottom one is chiral)
Figure 110. HPLC spectra of 2h

2h (The top one is racemic, and the bottom one is chiral)
Figure 111. HPLC spectra of 2i

2i (The top one is racemic, and the bottom one is chiral)
Figure 112. HPLC spectra of 2j

2j (The top one is racemic, and the bottom one is chiral)
Figure 113. HPLC spectra of 2k

2k (The top one is racemic, and the bottom one is chiral)
Figure 114. HPLC spectra of 2l

2l (The top one is racemic, and the bottom one is chiral)
Figure 115. HPLC spectra of 2m

2m (The top one is racemic, and the bottom one is chiral)
Figure 116. HPLC spectra of 2n

2n (The top one is racemic, and the bottom one is chiral)
Figure 117. HPLC spectra of 2o

2o (The top one is racemic, and the bottom one is chiral)
Figure 118. HPLC spectra of 2p

2p (The top one is racemic, and the bottom one is chiral)
Figure 119. HPLC spectra of 2q

2q (The top one is racemic, and the bottom one is chiral)
Figure 120. HPLC spectra of 2r

2r (The top one is racemic, and the bottom one is chiral)
Figure 121. HPLC spectra of 2s

(The top one is racemic, and the bottom one is chiral)

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<td>95.0994</td>
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</tbody>
</table>
Figure 122. HPLC spectra of 2t

2t (The top one is racemic, and the bottom one is chiral)
Figure 123. HPLC spectra of 2u

2u (The top one is racemic, and the bottom one is chiral)
Figure 124. HPLC spectra of 2v

2v (The top one is racemic, and the bottom two are chiral)

This one is prepared from cis-substrate (Z-1v).
Figure 125. HPLC spectra of 3v

3v (The top one is racemic, and the bottom one is chiral)
Figure 126. HPLC spectra of 3a

3a (The top one is racemic, and the bottom one is chiral)
Figure 127. HPLC spectra of 4a

4a (The top one is racemic, and the bottom one is chiral)

Table: HPLC Data

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<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*cm]</th>
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<th>Area [%]</th>
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Table: HPLC Data

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6. X-ray Crystallographic Data

Figure 128. X-Ray Crystallographic Data for Compound(R)-4a

![Image of molecular structure]

Structure factors have been supplied for datablock(s) (CCDC: 2076650)

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